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Organo-Phosphorus Compounds

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Technical Report No. 6

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Contract Nos. N90nr-87500 and -87501

Project No. NR 035 205

Period Covered: September 1, 1950 to November 30, 1950

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SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

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SHELL DEVELOPMENT COMPANY

EMERYVILLE, CALIFORNIA

TELEPHONE OLYMPIC 3-2100

February 16, 1951

COMMANDING OFFICER
U. S. Navy, Office of Naval Research
Branch Office
801 Donahue Street
San Francisco, California

Dear Sir:

Reference: Contract ONR:SF/14-3(23) N9onr-87501
Project No. NR 055 205

We enclose two copies of our sixth report under the subject contract which we have issued as Technical Report No. VI "Organo-Phosphorous Compounds". This report covers the period September through November, 1950.

By copies of this letter, distribution of this report is being made in accordance with prescribed distribution for Technical Reports as listed in the attachment hereto.

Yours very truly,

SHELL DEVELOPMENT COMPANY


T. W. Evans

AJLT/ec
Attachments

cc's on following pages

14
Report No. S-13255

6 ORGANO-PHOSPHORUS COMPOUNDS.

9 Technical Report No. 6, 1 Sep-30 Nov 50.

See

Department of the Navy
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11 30 Nov 50
12 47p.

Period Covered: September 1, 1950 to November 30, 1950

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Contract No. N9onr-87500

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SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

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Report No. S-13255

SHELL DEVELOPMENT COMPANY
Emeryville, California
January 23, 1951

Contract No. N9onr-87500
-87501

Project No. NR 055 205

ABSTRACT

↙ The present Technical Report No. VI, covering the quarter September 1 to November 30, 1950, in continuation of the trend developed in the previous quarter, discusses the preparation and evaluation of phosphonates as potential lubricants and/or hydraulic fluids, to the exclusion of phosphinates and phosphine oxides, as the latter two classes of compounds have not appeared promising. The total numbers of preparations of this period are as follows: phosphine oxides, 0 (total for six quarters, 10); phosphinates, 0 (19); phosphonates, 18 (53); phosphates, 0 (2); miscellaneous, 1 (11); grand total, 19 (95). The number of phosphonates (18) can be broken down in this manner: 2 monophosphonates for use as intermediates; 3 monophosphonates for evaluation; 6 polyphosphonates for evaluation, of which 4 were bis-compounds; and 7 repeated syntheses of promising compounds as "bottoms-products", that is, the materials were not distilled. The latter were evaluated to ascertain whether or not they still retained their favorable characteristics on elimination of the tedious molecular distillation to which they had previously been subjected. In general, this they appeared to do very satisfactorily in the bench scale evaluations which are continuing. Motor Laboratory evaluations have been accelerated, still using commercial materials for orientation studies in Pesco gear pumps, cold and hot Lauson engines and spur gear load carrying capacity tests. ↘ Larger scale preparations (ca. 5 gallons) are now underway to provide material for much more extensive testing of a few of the most attractive materials.

PREPARATIONS

I. Introduction and Summary

From the evaluation data presented in Technical Reports I through V it has become evident that of the following classes of organo-phosphorus compounds--phosphine oxides, monoalkane phosphinates, dialkanephosphinates, and phosphonates--the phosphonates show the most promise of application as lubricants and/or hydraulic fluids. When blended with additives, certain of the mono- and bis-phosphonates have shown some properties equal to or better than commercially available products.

In view of this evidence the majority of the present synthesis work has been devoted to the preparation of new phosphonates and to the synthesis of a number of promising phosphonates as bottoms-products. This latter effort has entailed the preparation of 200-300 cc. quantities of undistilled material in such a manner that the process could be carried out in a small pilot plant. In some cases the Lubricants and Fuels Department found these bottoms-products to be actually superior to the laboratory samples that had been carefully purified by distilling through a molecular still.

II. Derivatives of Phosphorous Acid

In carrying out the synthesis of a large number of the compounds described in earlier reports tributyl phosphite¹⁾ has been used as one of the starting materials. This phosphite was employed because it was then commercially available and experience in this laboratory on other problems had shown the n-butyl group to impart good rheological properties. In order to synthesize compounds of higher molecular weight another phosphite, tris (3,5,5-trimethylhexyl) phosphite, has been prepared for use as a starting compound.

A. Tris (3,5,5-trimethylhexyl) phosphite. (C₉H₁₉O)₃P

This ester was made by reacting 3,5,5-trimethylhexanol with phosphorus trichloride in the presence of pyridine.

A reaction flask, surrounded by a cooling bath at 0° to 15°C, was charged with 880 g. (6.1 moles) of 3,5,5-trimethylhexanol²⁾, 483 g. (6.1 moles) of pyridine and 1300 cc. of toluene. To this solution was added slowly with stirring 275 g. (2.0 moles) of phosphorus trichloride in 300 cc. of toluene. When addition was complete, the reaction mixture was allowed to stand overnight at room temperature, and then filtered to remove pyridine hydrochloride. After flashing off the toluene the residue

1) A recent letter from the du Pont Co. (11-14-50) advises that they no longer manufacture this compound.

2) Readily available as "nonyl" alcohol by the Oxo reaction.

was distilled from a Claisen flask. There was recovered 846 g. (1.84 moles) of product, boiling at 170-180°C at 0.1 mm. This represented a 91.8 per cent conversion on the charged phosphorus trichloride. Other properties of the compound are given in Table 1 and the bis-phosphonate prepared by reacting with bis (2-bromoethyl) ether is described in another section of this report.

III. Derivatives of Phosphonic Acid

From evidence presented in Status Report V it was shown that of the organo-phosphorus compounds studied the phosphonates showed the most promise of application as lubricants and hydraulic fluids. In view of this, synthesis work was devoted mainly to preparing mono- and polyphosphonates.

A. Monophosphonates

1. Bis(2-bromoethyl) benzenephosphonate. $C_6H_5PO(OCH_2CH_2Br)_2$
2. Bis(2-chloroethyl) benzenephosphonate. $C_6H_5PO(OCH_2CH_2Cl)_2$

These two compounds were prepared to use as intermediates in the preparation of a triphosphonate and to be evaluated themselves. They were made by reacting benzenephosphonic dichloride with the halohydrin in the presence of pyridine. The experiment for the chlorohydrin follows:

Into a flask equipped with a stirrer and cooling bath was charged 322 g. (4.0 moles) of ethylene chlorohydrin, 317 g. (4.0 moles) of pyridine and 1200 g. of toluene. To this was slowly added 370 g. (1.9 moles) of benzenephosphonic dichloride. When all the dichloride had been added, the mixture was allowed to stand overnight at room temperature. After filtering the pyridine hydrochloride, the solution was washed and then after removal of the toluene, was distilled through a molecular still. The halide appeared to hydrolyze easily on treatment with dilute sodium hydroxide. Other properties are given in Table 1.

3. Di-n-butyl 3,5,5-trimethylhexanephosphonate. $C_9H_{19}PO(O_2C_4H_9)_2$

The 3,5,5-trimethylhexyl derivatives already prepared and described have shown good oxidation and corrosion characteristics. To study a compound with this group attached directly to the phosphorus atom, tributyl phosphite has been reacted with 3,5,5-trimethylhexyl bromide. The method used was the low pressure technique described in Technical Report V, page 5. The properties of the product are given in Table 1.

4. Bis(3,5,5-trimethylhexyl) benzenephosphonate.
 $C_6H_5PO(OC_9H_{19})_2$

An additional trimethylhexyl derivative was obtained by reacting benzenephosphonic dichloride with 3,5,5-trimethylhexanol. The Lubricants and Fuels Department will compare the properties of this ester with those of the bis(3,5,5-trimethylhexyl) "isooctene" phosphonate given in the last report.

The method used in the synthesis of this ester was similar to that described in this report on page 2. Properties of the compound are given in Table 1.

5. Di-n-butyl "styrene" phosphonate. $(C_4H_9O)_2POCH=CH \cdot C_6H_5$

This monophosphonate was prepared both as a distilled and as a "bottoms-product", being made from n-butyl alcohol and "styrene" phosphonic dichloride. The properties of the ester are given in Table 1.

B. Polyphosphonates

Prior work has shown that the diphosphonates show marked superiority over the monophosphonates with regard to low flammability. An additional number of this class of compounds has been synthesized along with a triphosphonate and a polymer.

1. Bis-1,2-[2-(di-n-butyl phosphono)ethoxy]ethane.
 $[(C_4H_9O)_2-PO-C_2H_4OCH_2-]_2$

It is well known that the polyethers of ethylene glycol have good viscosity indices, and that the ether linkages are quite stable. To incorporate this into a diphosphonate, a reaction between tributyl phosphite and triglycol dichloride has been carried out. The compound is described in Table 1.

In this experiment, where the Arbuzov reaction was being carried out with a chloro derivative, it was necessary to heat the reaction at 230-260°C in order to split out butyl chloride. From a charge of 187 g. (1.0 moles) of triglycol dichloride $(Cl \cdot CH_2 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot Cl)$ and 750 g. (3.0 moles) of tributyl phosphite was recovered, 327 g. of product boiling at 140°C at 0.017 mm.

2. Bis [2-(bis(3,5,5-trimethylhexyl) phosphono)ethyl] ether.
 $[(C_9H_{19}O)_2-PO-C_2H_4]_2O$

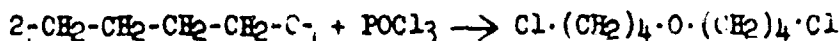
A sample of bis [2-(di-n-butyl phosphono)ethyl] ether has been evaluated and found to possess one serious drawback in that it is not miscible with Acryloid viscosity index improvers. In an attempt to remedy this, we

have synthesized bis [2- [bis (3,5,5-trimethylhexyl) phosphono]ethyl] ether by reacting tris (3,5,5-trimethylhexyl) phosphite³⁾ with bis (2-bromoethyl) ether at 180° to 200°C and 17 mm. pressure. The product, distilling at 182-184°C at 0.011 mm., was formed in a yield of over 95 per cent and is described in Table 1.

3. Bis [4-(di-n-butyl phosphono)butyl] ether.
 $[(C_4H_9O)_2-PO-C_4H_9]_2O$

Another possible method of improving the diphosphono ethers described above is to replace the diethyl ether portion of the molecule with dibutyl ether. This was accomplished by reacting bis(4-chlorobutyl) ether with tributyl phosphite.

The bis(4-chlorobutyl) ether, $(Cl-CH_2-CH_2-CH_2-CH_2)_2O$, was prepared by the method of Alexander and Schniepp⁴⁾ which consisted in treating tetrahydrofuran with phosphorus oxychloride in the presence of sulfuric acid.



It was found that this dichlorobutyl ether reacted very slowly with tributyl phosphite below 250°C and rapidly at 265-275°C. The bis-phosphonate, after distillation and treatment with 1 N sodium hydroxide, was a light, oily liquid with an acid number of less than 0.1. Its other properties are given in Table 1.

4. Bis[2-(di-n-butyl phosphono)ethyl] benzene-phosphonate.
 $C_6H_5-PO[OCH_2-CH_2-PO(OC_4H_9)_2]_2$

In order to investigate the properties of a compound containing three phosphorus atoms we have synthesized a triphosphonate. By reacting tributyl phosphite (263 g., 1.05 moles) with bis(2-bromoethyl) benzene-phosphonate (130 g., 0.35 moles) at 160°C and reduced pressure there was formed 145 g. of the desired product. The triphosphonate was an oily liquid boiling at 168-190°C at 0.014 mm. pressure. In Table 1 are given the other properties of the compound.

5. Chloroparaffinphosphonate. $Cl_x \cdot R \cdot PO(OC_4H_9)_2$

It should be possible to prepare a somewhat different type of phosphonate by reacting a long chain chlorinated paraffin with either tributyl phosphite or sodium dibutyl phosphite. If all of the chlorine atoms reacted, then one would obtain a polyphosphonate, otherwise a chlorine-containing product would result. One experiment has been performed by reacting a chlorinated paraffin, containing 30 per cent chlorine, with sodium dibutyl phosphite.

3) This compound is described on page 2 of this report.

4) J. Am. Chem. Soc. 70, 1839 (1948).

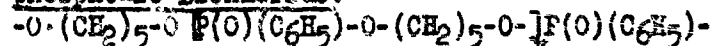
A solution of sodium dibutyl phosphite was prepared by dissolving 19 g. (0.82 moles) of sodium in 194 g. (1.0 moles) of dibutyl phosphite in 1000 cc. of toluene. To this solution, at 105-112°C, was added 236 g. (2.0 g-atoms of chlorine) of Chlorofin 15.5) After refluxing for 24 hours, water was added to dissolve the sodium chloride which had separated. The water layer was discarded, and after washing twice with water, the toluene was flash-distilled to recover 307 g. of a yellow oil. To remove any free acidity and easily hydrolyzable impurities, 291 g. of this oil was refluxed for 2 hours with 300 cc. of 1.0 N sodium hydroxide. The recovered product weighed 256 g. after drying and had an acid number of 0.02.

Of interest is a comparison of properties of the original chloroparaffin and the chloroparaffinphosphonate.

	Chlorofin 15	Chloroparaffinphosphonate
vis. cs. 100°F	94.8	29.2
vis. cs. 210°F	10.5	5.17
VI	101	119
% Cl	30.0	19.1

Other properties of the chloroparaffinphosphonate are given in Table 1.

6. Polyphosphonate from 1,5-Pentanediol and Benzenephosphonic Dichloride.



One experiment has been made to obtain a polyphosphonate by reacting a glycol with an alkanephosphonic dichloride. From 1,5-pentanediol and benzenephosphonic dichloride was obtained a very thick, viscous product that would hardly pour at room temperature. The molecular weight of the product indicates it to be a tetramer. Further work is planned in order to obtain a less viscous material.

IV. "Bottoms-Products"

- A. Bis(3,5,5-trimethylhexyl) benzenephosphonate. $C_6H_5PO(OC_9H_{19})_2$
- B. Bis(3,5,5-trimethylhexyl) "isooctene"phosphonate.
 $C_8H_{15}PO(OC_9H_{19})_2$
- C. Dibutyl benzenephosphonate. $C_6H_5PO(OC_4H_9)_2$
- D. Dibutyl "styrene"phosphonate. $C_6H_5CH=CHPO(OC_4H_9)_2$

5) Chlorofin 15 was purchased from Hooker Electrochemical Co. and contained 30 per cent chlorine.

- E. Bis (7-methyl-4-thiaoctyl) benzenephosphonate.
 $C_6H_5PO(OC_3H_6SC_5H_{11})_2$
- F. Pis [2-(di-n-butyl phosphono)ethyl] ether. $[(C_4H_9O)_2POCH_2CH_2]_2O$
- G. Bis-1,6-(di-n-butyl phosphono)hexane. $[(C_4H_9O)_2POCH_2-CH_2-CH_2-]_2$

As this contract goes into its second year it is now planned that an increasing number of the best laboratory products will be synthesized on a larger scale for more complete evaluation by both the Motor Laboratory and the Fuels and Lubricants Department. As has been described in the earlier Technical Reports, the materials evaluated by bench scale were purified at one step by means of a distillation--often in a molecular still. This would probably present some difficulty on large-scale manufacture because of the high boiling points and the necessity of keeping the acid number low.

With the possibility that those products chosen to be tested on a larger scale could be prepared as undistilled ("bottoms") products, we have made a number in this manner for comparative, bench-scale testing. The compounds were prepared by one of two methods:

- (a) Reaction of an alkanephosphonic dichloride with an alcohol in the presence of pyridine, or
- (b) The reaction of tributyl phosphite with a dihalide.

Typical experiments are described below and the properties of all of the bottoms-products are given in Table 1.

Bis(3,5,5-trimethylhexyl) "isooctene"phosphonate.

Into a flask equipped with a stirrer and surrounded with a cooling bath were charged 576 g. (4.0 moles) of 3,5,5-trimethylhexanol, 237 g. (3.0 moles) of pyridine and as a diluent 1000 cc. of toluene. To this cooled solution (0°-5°C) was slowly added 231 g. (1.0 moles) of "isooctene"phosphonic dichloride. When addition was complete, the reaction was heated at 95-100°C for 3 hours, and then the product was recovered by diluting with water to dissolve the pyridine hydrochloride. The water layer was separated and the toluene solution again washed with water. The toluene was distilled off and the reaction mixture was stabilized by heating at 180°C at 5 mm. pressure. In order to remove any acids or easily hydrolyzable impurities, 436 g. of this stabilized residue was refluxed at atmospheric pressure (102°C) with 500 cc. of 1.3 N sodium hydroxide solution. The aqueous phase was drained and 300 cc. of benzene was added to the product. This benzene solution was washed three times with hot water and after flashing off the benzene, the bis(3,5,5-trimethylhexyl) "isooctene"phosphonate was dried at 150°C and 5 mm. pressure.

(Table 1 follows.)

Table 1. ORGANO-PHOSPHORUS COMPOUNDS

REFERENCE	COMPOUND	n _D ²⁰		d ₄ ²⁰	n _D ²⁰	ANALYSIS				MOL. WT.		REMARKS
		Calcd.	Found			Calcd.	Found	Calcd.	Found	Calcd.	Found	
DERIVATIVES OF PHOSPHOROUS ACID												
W-18-35	Na[3,5,5-trimethylphenyl] phosphite	190-190	0.1	0.862	1.446	-	-	6.72	7.1	-	-	-
DERIVATIVES OF PHENEMIC ACID												
W-18-35	Na[3,5,5-trimethylphenyl] phosphite	190-190	0.010	1.6865	1.5254	-	-	8.35	8.6	-	-	Hydrolyzes in dil. sodium hydroxide
W-18-36	Na[3,5,5-trimethylphenyl] phosphite	80-85	0.010	1.3690	1.2672	-	-	11.1	10.9	-	-	-
W-18-37	Na[3,5,5-trimethylphenyl] phosphite	117-121	0.05	0.9199	1.4405	-	-	9.49	9.5	-	-	0.05
W-18-38	Na[3,5,5-trimethylphenyl] phosphite	115	0.012	0.9715	1.4874	-	-	7.26	7.27	-	-	0.042
W-18-39	Na[3,5,5-trimethylphenyl] phosphite	161-162	0.5	1.0591	1.5167	64.8	55.0	8.45	10.5	10.7	296	0.08
W-18-40	Na[3,5,5-trimethylphenyl] phosphite	140-142	0.030	1.7498	-	-	-	12.35	1.1	-	-	0.20
W-18-41	Na[3,5,5-trimethylphenyl] phosphite	182-184	0.011	0.9598	1.4948	-	-	9.91	8.8	-	690	0.10
W-18-42	Na[3,5,5-trimethylphenyl] phosphite	125-170	0.014	1.0194	1.4521	-	-	12.05	11.8	-	-	0.04
W-18-43	Na[3,5,5-trimethylphenyl] phosphite	160-190	0.014	1.1055	1.4777	-	-	15.0	15.5	-	-	0.02
W-18-44	Na[3,5,5-trimethylphenyl] phosphite	-	-	1.0064	1.4690	-	-	-	4.16	-	-	0.02
W-18-45	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	13.7	12.9	0	694 (calculated)	-
DERIVATIVES OF PHENEMIC ACID												
W-18-46	Na[3,5,5-trimethylphenyl] phosphite	-	-	0.9703	1.4750	70.5	70.4	10.4	10.8	7.26	7.64	0.05
W-18-47	Na[3,5,5-trimethylphenyl] phosphite	-	-	0.9165	1.4555	70.5	70.5	11.9	12.5	6.98	7.15	0.10
W-18-48	Na[3,5,5-trimethylphenyl] phosphite	-	-	1.0995	1.4878	68.2	68.7	8.32	8.7	11.4	11.5	0.05
W-18-49	Na[3,5,5-trimethylphenyl] phosphite	-	-	1.0591	1.5167	64.8	65.0	8.45	8.8	10.5	10.7	0.08
W-18-50	Na[3,5,5-trimethylphenyl] phosphite	-	-	1.0513	1.5122	-	-	-	-	6.90	6.80	0.10
W-18-51	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	36.5	32.4	9.26	9.7	13.5	13.7	0.09
W-18-52	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	13.2	12.8	0.02
W-18-53	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
DERIVATIVES OF PHENEMIC ACID												
W-18-54	Na[3,5,5-trimethylphenyl] phosphite	-	-	0.9703	1.4750	70.5	70.4	10.4	10.8	7.26	7.64	0.05
W-18-55	Na[3,5,5-trimethylphenyl] phosphite	-	-	0.9165	1.4555	70.5	70.5	11.9	12.5	6.98	7.15	0.10
W-18-56	Na[3,5,5-trimethylphenyl] phosphite	-	-	1.0995	1.4878	68.2	68.7	8.32	8.7	11.4	11.5	0.05
W-18-57	Na[3,5,5-trimethylphenyl] phosphite	-	-	1.0591	1.5167	64.8	65.0	8.45	8.8	10.5	10.7	0.08
W-18-58	Na[3,5,5-trimethylphenyl] phosphite	-	-	1.0513	1.5122	-	-	-	-	6.90	6.80	0.10
W-18-59	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	36.5	32.4	9.26	9.7	13.5	13.7	0.09
W-18-60	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	13.2	12.8	0.02
W-18-61	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-62	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-63	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-64	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-65	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-66	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-67	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-68	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-69	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-70	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-71	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-72	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-73	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-74	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-75	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-76	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-77	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-78	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-79	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-80	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-81	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-82	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-83	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-84	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-85	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-86	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-87	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-88	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-89	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-90	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-91	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-92	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-93	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-94	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-95	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-96	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-97	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-98	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-99	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-100	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-101	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-102	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-103	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-104	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-105	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-106	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-107	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-108	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-109	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-110	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-111	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-112	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-113	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-114	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-115	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-116	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-117	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-118	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-119	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-120	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-121	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-122	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-123	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-124	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-125	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-126	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-127	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-128	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-129	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-130	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-131	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-132	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-133	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-134	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-135	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-136	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-137	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-138	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-139	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-140	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-141	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-142	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-143	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-144	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-145	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-146	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-147	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-148	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-149	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-150	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-151	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-152	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-153	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-154	Na[3,5,5-trimethylphenyl] phosphite	-	-	-	-	-	-	-	-	0	0	-
W-18-155	Na											

This ester was very light yellow in color (Gardner Color 1) and had an acid number of 0.10. From this treatment was recovered 387 g. (0.87 moles) of product which represented an 87.0 per cent conversion to product based on the charged "isooctene"phosphonic dichloride.

Bis[2-(di-n-butyl phosphono)ethyl] ether.

Into a kettle attached to a fractionating column was placed 750 g. (3.0 moles) of tributyl phosphite. After heating to 160°C at 40 mm. pressure, there was slowly added 232 g. (1.0 moles) of bis(2-bromoethyl) ether. The butyl bromide formed during this Arbuzov reaction was recovered in a cold trap. When no further butyl bromide was liberated, the reaction mixture was stabilized by heating to 156°C at 5.0 mm. pressure. A sample of 482 g. of this crude product was heated under reflux with 500 cc. of 1.2 N sodium hydroxide. After refluxing for 2.5 hours (when intermittent titrations showed that no further caustic was being consumed), the aqueous phase was separated and the product washed with hot water. The bisphosphonate was dried by heating at 150°C and 5 mm. pressure. There was recovered 392 g. of product which had an acid number of 0.09 and a Gardner Color of 2. This represented an 85.5 per cent conversion based on the charged bis(2-bromoethyl) ether.

V. Catalysts for the Arbuzov Reaction.

It is well known that in general the ease of reaction between an alkyl halide and a trialkyl phosphite depends to a large extent on the nature of the alkyl halide. Thus, in the n-butyl halide series, n-butyl iodide reacts easier than the bromide which in turn reacts easier than the chloride. So far during this program a number of alkyl chlorides have been reacted with certain phosphites and this has required the use of high temperatures and long reaction times. As a consequence of these reaction conditions, yields of product from the Arbuzov reaction using chlorides have been found to be low.

With the possibility that the Arbuzov reaction could be catalyzed by the use of certain metal salts to such an extent that it would be possible to employ the less-expensive chlorides, the following tests were carried out:

Tributyl phosphite has been reacted with 2-ethylhexyl chloride alone and in the presence of certain metals. The experiments were carried out by heating the reactants to 200°C in a kettle attached to a fractionating column. Any butyl chloride formed during the reaction was recovered and measured in order to follow the course of the reaction. From the data shown in Figure 1 it may be seen that 2-ethylhexyl chloride underwent substantially no reaction. The addition of potassium iodide, copper bromide or copper iodide to the mixture (2 g. catalyst for 100 g. reactants) caused the reaction rate to increase, copper iodide being the most effective. However, it may be seen that none of the catalysts caused the 2-ethylhexyl chloride to react as rapidly as 2-ethylhexyl bromide.

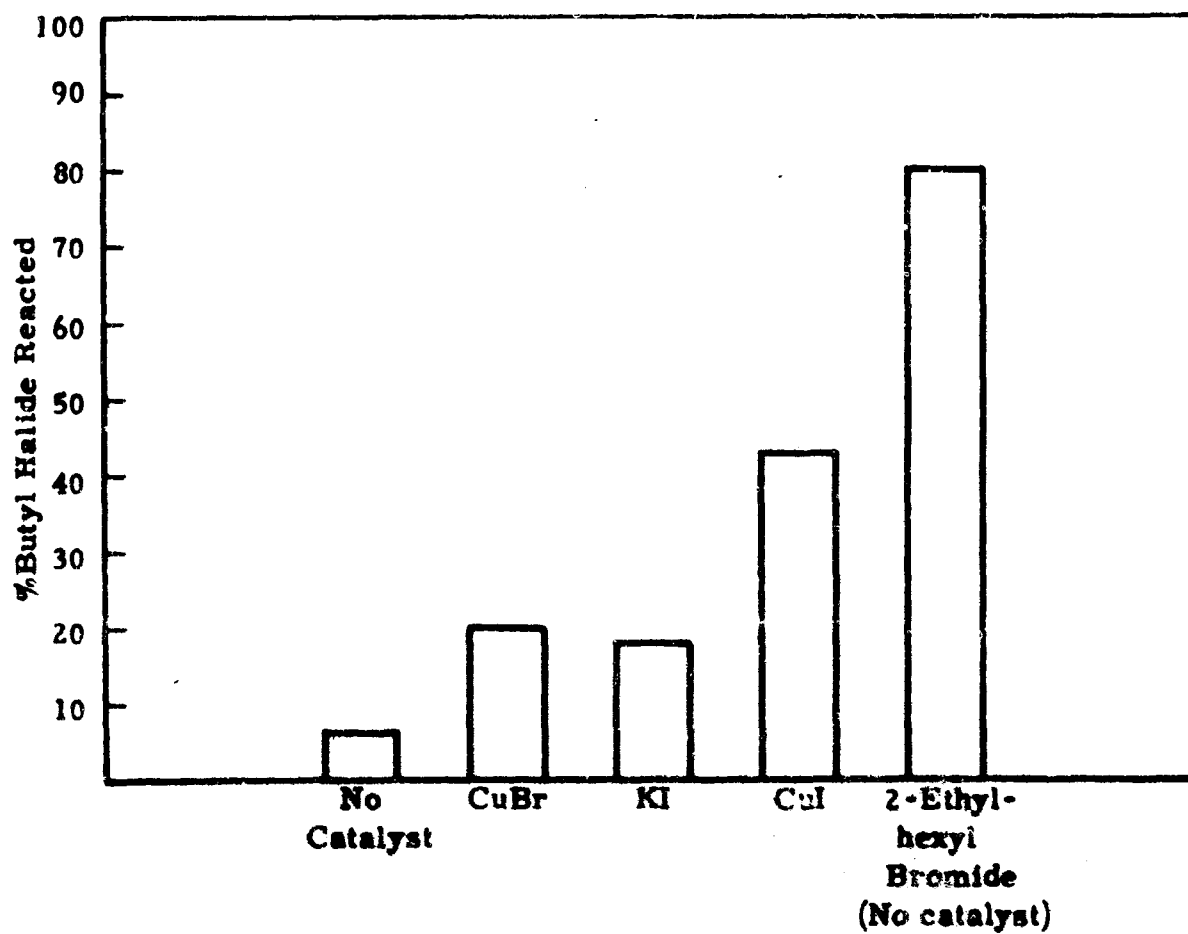
(Figure 1 follows.)

**Figure 1. REACTION OF 2-ETHYLHEXYL CHLORIDE WITH TRIBUTYL
PHOSPHITE IN THE PRESENCE OF CERTAIN CATALYSTS**

Reaction Time 7 hrs.

Reaction Temp. 200°C

(The 2-ethylhexyl bromide was reacted 1.5 hours)



BENCH SCALE EVALUATIONS

I. Introduction and Summary

As the synthesis program on new compounds begins to taper off and certain materials show promise for further evaluation in larger quantities (ca. 5 gals.), there has been an increase in effort toward the investigation of thickeners and inhibitors to improve the already attractive properties of the selected organo-phosphorus compounds.

For the preparation of technical grade or bottoms-products, compounds were chosen from several viscosity levels and types of structure. Thus, a monophosphonate of fairly low viscosity but good nonflammability was selected together with several monophosphonates with longer alkyl chains. Several bisphosphonates, comparable in viscosity to some of the long chain monophosphonates, were also included. The emphasis on the phosphonates and possibly bisphosphates has been continued in this period. Although the bisphosphonates appear attractive, certain problems of preparation on a larger scale have delayed their study in favor of some of the more viscous monophosphonates. In general the technical grade preparations have compared very favorably with the earlier, molecularly-distilled products. However, the two technical grade bisphosphonates so far prepared had poor thermal stability, while all preparations of monophosphonates were satisfactory on this score.

Among the new molecularly-distilled preparations with attractive properties were bis[4-(dibutyl phosphono)butyl]ether, bis[2-(dinonyl phosphono)ethyl]ether, bis[2-(dibutyl phosphono)ethyl] benzenephosphonate, bis-1,2-[2-(dibutyl phosphono)ethoxy]ethane and dibutyl nonanephosphonate. A sample of pentamethylene tetra-n-butyl diphosphate from Victor Chemical Works also had some outstanding properties.

II. Evaluation

A. Summaries of Specific Properties on New Compounds

The data obtained on the new compounds are summarized in Table 2 using the same form employed in previous reports. They are discussed under the specific properties shown in the heading of the table. Of the new compounds examined, there were four monophosphonates, one monophosphinate, and one bisphosphinico, one trisphosphono and three bisphosphono compounds. A new preparation of dioctyl "styrene"phosphonate, of very low acidity, and a diphosphate, both from Victor Chemical Works, were also included in the bench-scale evaluations. In addition, six bottoms or technical grade products, in addition to the one technical preparation previously discussed in V have also been evaluated.

1. Acidities

Most of the compounds had acidities less than 0.10 mg. KOH/g. The exceptions were bis-2-chloroethyl benzenephosphonate, acid no. = 0.45, and bis[2-(dibutyl phosphono)ethyl] benzenephosphonate, acid no. = 0.80. Several others had borderline acidities of 0.10.

2. Pour Points

The majority of the compounds had low pour points, -65°F or lower, and are not further discussed. Included in the few which had high pour points were chloroparaffinphosphonate, $+20^{\circ}\text{F}$, and bis[2-(butyl p-chlorobenzene phosphinico)ethyl]ether, $+15^{\circ}\text{F}$. The viscous bis[2-(dinonyl phosphono)ethyl]ether had a pour point of -30°F but the less viscous (but negative VI) samples of bis-2-chloroethyl benzenephosphonate and butyl p-chlorobenzene(butane)phosphinate had pour points of -35 and -45°F . The highest pour point of the technical grade preparations was -55°F , which is still fairly satisfactory.

3. Viscosities

Viscosities were determined at 100°F and 210°F on all the samples, and at -40°F on those with pour points of -45°F or lower. Since the majority of the viscosities at -40°F were rather large (only three were less than 1000 cs.), viscosities at lower temperatures (such as -60°F) were not attempted on this series.

The sample of lowest viscosity was the dibutyl benzenephosphonate, bottoms-product. The pure dibutyl nonanephosphonate was only slightly more viscous at 100°F and 210°F . However the -40°F viscosity of the latter was almost double that of the dibutyl benzenephosphonate. These two products are similar in flammability, oxidation, corrosion and thermal stability characteristics. They differ considerably in wear in the 4-ball apparatus.

The most viscous product was the bis[2-(butyl p-chlorobenzene-phosphinico)ethyl]ether which falls in the SAE 40 range. Unfortunately, the high pour point, negative VI and poor thermal stability are serious liabilities and do not offset the excellent low flammability and interesting viscosity of this compound. The next-most viscous compound in Table 2 was the bis[2-(dinonyl phosphono)ethyl]ether which falls in the SAE 20 range. This compound looks much more attractive from the standpoint of flammability, thermal stability, inhibitor susceptibility, miscibility with polymers (Acryloid) and wear. The corresponding "octyl" derivative has been prepared for early evaluation. All of the remaining preparations in the table have viscosities at 100°F between 12 and 30 cs.

The viscosities which were measured at -40°F ranged from 363 cs. for the dibutyl benzenephosphonate to 82,230 cs. for the butyl p-chlorobenzene-(butane)phosphinate. The new batch of dioctyl "styrene"phosphonate (Victor Chemical) had a viscosity of 77,450 cs. at -40°F .

4. Viscosity Indices

The highest VI (132, Dean and Davis) in the table was displayed by the Victor pentamethylene tetrabutyl diphosphate which incidentally also had a very low pour point (below -65°F). The next highest VI, 140, was shown with the bis[4-(dibutyl phosphono)butyl]ether which also had a very low pour point, -80°F . Six other preparations had viscosity indices above 100, ranging from

113 to 128. Of the six preparations having viscosity indices of 0 or lower, all contained either halogen, aromatics or both. Five other preparations had viscosity indices between 70 and 90 and of these, three were benzenephosphonates. The presence of one benzene ring does not therefore necessarily result in a low VI. However, all of the "styrene"phosphonates had low VI.

The Hardiman and Nissan viscosity indices were also determined and are given in Table 2. For the very low viscosity samples (less than 3.2 cs. at 210°F) the Hardiman and Nissan VI is appreciably higher than that of Dean and Davis, while in the higher viscosity ranges, with a few exceptions, the H. and N. VI is usually lower than the D. and D. VI.

The ratio of viscosity at 100°F, in cs., to viscosity at 210°F has also been given in Table 2. The ratio corresponds more closely to the viscosity index in the Hardiman and Nissan system than to the Dean and Davis VI. For example, the lowest viscosity samples, dibutyl benzene- and dibutyl nonanephosphonate, rated high in both ratio and H. and N. VI. Further, if the nineteen compounds in the table are listed in sequence according to their viscosity-temperature behavior as rated by these three methods, the ratio agrees (within 3 units of same rating) with the H. and N. VI in 14 cases and with the D. and D. VI in 10 cases. The two VI methods agree in 15 out of 19 cases.

5. Flammability

The semi-micro open cup (see III-18 for description) and the pipe-cleaner test (II-15) have been used to test flammability of the pure compounds, commercial products and technical grade preparations. In two cases the sample size was insufficient to run the semi-micro flash and fire points. Except for the greater variation in fire points with the current data, plots relating flash and fire points in either test are similar to Figures 1 and 2 of Technical Report No. IV. Several samples, including the halogen-containing phosphonates and phosphinates as well as the trisphosphonate, give better pipe-cleaner fire points than would be expected from their micro-open cup behavior. All of the compounds in Table 2 have flammabilities in the pipe-cleaner test equal to or better than HS-1, the flammability reference in AMS-3150A. The halogen-containing organo-phosphorus compounds are especially good in this regard but their other qualities make them generally unattractive for use as hydraulic fluids. The very viscous bis[2-(butyl p-chlorobenzenephosphinico)ethyl]ether had the highest pipe-cleaner results obtained to date on any organo-phosphorus compound.

6. Thermal Stability

It is significant that most of the technical grade or bottoms-products had satisfactory thermal stability whereas the previous first technical preparation of the bis-1,6-(dibutyl phosphono)hexane (bottoms) had poor thermal stability (see Table 2 of V). However, the thermally stable bottoms-products are all monophosphonates and the only additional bisphosphonate in this classification was also unstable. The bis[2-(butyl p-chlorobenzenephosphinico)ethyl]ether and bis[2-(dibutyl phosphono)ethyl]ether (bottoms-product) had poor thermal stability while the bis[2-(dibutyl phosphono)ethyl] benzenephosphonate was borderline.

(Table 2 follows.)

Table 2. PHYSICAL AND CHEMICAL PROPERTIES OF ORGANO-PHOSPHORUS COMPOUNDS

Compound	Formula	Refractive Index	Mn	Mw	Pn	Viscosity, η		R _{sp}	Thermal Stability		Solubility		Mechanical Properties		Thermal Conductivity	Thermal Expansion	Thermal Shrinkage
						100°C	200°C		Decomposition Temp. (°C)	Decomposition Weight %	Modulus of Elasticity (GPa)	Tensile Strength (MPa)	Impact Strength (kJ/m²)	Thermal Conductivity (W/mK)			
Polystyrene	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Polystyrene (cross-linked)	$(C_6H_5)_n$	1.05	105	105	105	0.01	0.01	1.05	250	10	0.01	0.01	0.01				

6. Above an Absolute Record for 3.6.5. Since the first time on 3.6.5. the first time on 3.6.5.

Several others, which gave less than five per cent change in viscosity at 210°F, exhibited appreciable change in VI, although this may indicate an erroneous viscosity at 100°F either before or after the test.

7. Corrosion and Oxidation Stability

As usual, the compounds have run the gamut from very stable to very unstable in the small-scale oxidation-corrosion test.

The compounds which gave satisfactory stability without inhibitors were dibutyl 3,5,5-trimethylhexanephosphonate, a new sample of dioctyl "styrene"phosphonate from Victor, dibutyl benzenephosphonate (bottoms), dibutyl "styrene"phosphonate, both pure and bottoms-products, and bis[4-(dibutyl phosphono)butyl]ether.

Compounds with intermediate oxidation and corrosion stability were the bis[2-(dibutyl phosphono)ethyl]ether (bottoms), bis-1,2-[2-(dibutyl phosphono)ethoxy]ethane, bis[2-(butyl p-chlorobenzenephosphinico)ethyl]ether and bis(7-methyl-4-thiaoctyl) benzenephosphonate.

Two of the nonyl derivatives, bis[2-(dinonyl phosphono)ethyl]ether and dinonyl "isooctene"phosphonate, gave low corrosion but very high oxidation.

Compounds exhibiting both high oxidation and corrosion were butyl p-chlorobenzene(butane)phosphinate, pentamethylene tetra-n-butyl diphosphate (from Victor Chemical), "chloroparaffin"phosphonate, bis[2-(dibutyl phosphono)ethyl] benzenephosphonate, bis(2-chloroethyl) benzenephosphonate and the dinonyl benzenephosphonates, both pure and bottoms-products.

In the section on inhibitors it will be shown that the high degree of oxidation and corrosion exhibited by the last compound in the above list can be controlled.

8. Wear and Friction

The 4-ball wear data on the compounds in Table 2 show a considerable spread in wear with only a small variation in friction coefficient. The lowest wear of any compound in this table was found for the new batch of dioctyl "styrene"phosphonate with the dinonyl "isooctene"phosphonate (bottoms) and dibutyl nonanephosphonate only slightly higher in wear. As previously noted, all of the bisphosphonates and the triphosphonate in this table gave high wear with one exception. This exception was the bis[2-(dinonyl phosphono)ethyl]ether where the longer alkyl chain on the ends of the molecule is apparently critical. Long chains between the phosphorus atoms have not been beneficial in reducing wear in the compounds so far studied. This difference in chain length is also apparent in the monophosphonates if one compares the wear from dibutyl benzenephosphonate with that from the corresponding dinonyl benzenephosphonate. Also the wear for dibutyl nonanephosphonate falls between that for dibutyl n-octanephosphonate and dibutyl 2-ethylhexanephosphonate previously reported (see Table 2, V). The nonyl or nonane group referred to in this work is the 3,5,5-trimethylhexyl or -heptane.

Therefore, the chain length is, of course, the same as that of the 2-ethyl-hexyl group but the added methyl side chain appears to have a beneficial effect also.

The high wear found for bis(7-methyl-4-thiaoctyl) benzenephosphonate appears out of line since the corresponding "isooctene"phosphonate gave low wear (see Table 2, V).

The wear with the two dibutyl "styrene"phosphonate samples was intermediate between the high wear of dibutyl benzenephosphonate and the low wear of dioctyl "styrene"phosphonate. The "chloroparaffin"phosphonate, prepared by reaction of Chlorofin 15 (Hooker Electrochemical) containing 30% chlorine with tributyl phosphite, gave much higher wear, 0.67 mm., than that for the original batch of Chlorofin 15, which gave a scar diameter of 0.44. The residual chlorine content in the reaction product may be contributory to the wear observed.

The coefficient of friction values for most of the preparations were between 0.10 and 0.13. The bis(2-chloroethyl) benzenephosphonate gave a low friction value, 0.07, as did the product obtained from this intermediate, the bis[2-(dibutyl phosphono)ethyl] benzenephosphonate. On the other hand, bis[2-(dibutyl phosphono)ethyl]ether (bottoms) and bis-1,2-[2-(dibutyl phosphono)ethoxy]ethane were slightly above average in friction coefficient.

B. Comparison between Properties of Pure Compounds and Technical Grade Products.

Since the larger-scale production of the more promising compounds developed under this contract must necessarily eliminate some of the steps in preparation of the pure compounds, such as the molecular distillation, a group of products has been prepared as technical grade or bottoms products. The impurities in these preparations may include unreacted initial ingredients, (if sufficiently high boiling), as well as polymers or side-reaction products. The effect of such contaminants on physical and chemical properties may be shown by the data in Table 3.

In general the bottoms-products compared closely with the pure compounds in regard to viscosity, VI, pour points, flammability, and thermal, oxidation, and corrosion stabilities. One exception was the technical grade dinonyl "isooctene"phosphonate which had a higher viscosity, lower VI and much higher oxidation than that for the pure compound. Another exception was in regard to the flash point in the pipe-cleaner test. This property was consistently lower for all bottoms-products even though other types of flammability tests, including the pipe-cleaner fire point, showed no systematic variations between the pure and technical compounds.

In several instances the oxidation and corrosion stability of the bottoms-products was better than that of the pure compounds. In the case of the dibutyl benzenephosphonate where this was true, the pure compound was a preparation from Victor Chemical Works. It had an acid number of 0.44 and this may account for its poor oxidation-corrosion test.

Table 3. COMPARISON BETWEEN PROPERTIES OF TECHNICAL,
GRADE PREPARATIONS AND MOLECULARLY DISTILLED REFINED PRODUCTS

	Di n-Butyl Benzene-phosphonate		Dinonyl Benzene-phosphonate		Dinonyl "Isocetane"-phosphonate		Dibutyl "Styrene"-phosphonate		Bis(7-Methyl 4-Thiaoctyl) Benzene-phosphonate		Bis[2-(Dibutyl Phosphono) ethyl] Ether	
	Pure	Btms.	Pure	Btms.	Pure	Btms.	Pure	Btms.	Pure	Btms.	Pure	Btms.
Acid Neut. No.	0.14	0.05	0.04	0.05	0.02	0.10	0.02	0.08	0.02	0.10	0.04	0.09
Viscosity cs. at -40°F	312	362.6	33,680	27,860	14,770	26,840	18,730	18,430	7723	5840	2575	2071
" " at 100°F	4.92	5.17	21.64	21.07	18.49	24.30	15.62	15.28	18.70	18.64	14.47	13.31
" " at 210°F	1.58	1.63	4.03	3.95	3.75	4.33	2.88	2.86	3.91	3.93	3.31	3.16
" " index (L&D)	74	74	87	84	99	89	-11	-7	118	121	110	113
Pour Pt., °F	<-65	<-65	-60	-55	<-65	-65	-50	-65	<-65	<-65	<-65	<-65
Micro Flash	350	340	420	425	425	420	380	370	440	450	475	445
Micro Fire	435	435	505	520	490	490	480	480	495	505	550	545
Pipe {Flash	11	9	15	13	18	14	12	9	22	14	16	15
Cleaner {Fire	19	17	20	21	22	21	17	16	23	16	22	22
Thermal {Inc V210	0	0	1	1	0	0	1	1	5.5	1	3	9
Stability {VI change	+1	+1	+1	+8	0	0	+2	0	+8	+7	+11	+8
Small	3.35	0.60	13.52	11.96	0	1.08	0.84	1.56	17.0	4.80	2.96	2.40
Scale	0.16	0.08	14.64	0.20	0.04	0	0.04	0.24	2.0	3.68	0.64	1.04
Oxidation	0.16	0	0.08	0.04	0.04	0	0	0	0	0.04	0	0.04
Loss	0.12	0.04	5.36	0.48	0	0.44	0	0.20	0	6.04	5.84	1.68
Corrosion	0.08	0	0.16	0.04	+0.04	0	0	0	0	0	0.04	0.16
Test	0.5	0	96	60	1.5	104	0	3	15	5.5	6	6
Acid Neut. No.	2.03	0.13	44.3	47.2	0.05	73.8	0.28	0.69	4.5	4.22	1.03	1.01
Wear Scar, mm.	0.69	0.13	0.48	0.46	0.44	0.38	0.41	0.47	0.70	0.70	0.73	0.84
Friction μ	0.13	0.13	0.13	0.11	0.12	0.12	0.13	0.13	0.12	0.12	0.12	0.15

The dinonyl benzene- or "isooctene"phosphonates and dibutyl "styrene"phosphonates appeared to give lower wear than the other compounds shown in this table.

The improved flammability of the bisphosphono compounds over the monophosphonates is illustrated with the bis[2-(dibutyl phosphono)ethyl]ether in comparison with dibutyl "styrene"phosphonate or bis(7-methyl-4-thiooctyl) benzenephosphonate (which has comparable viscosity at 100°F) in the micro open-cup flash and fire points. The correlation between pipe-cleaner and open-cup apparatus with these compounds is not equal to the earlier results previously reported.

In general the very similar oxidation-corrosion results with either pure or bottoms product was very gratifying. The extreme difference in oxidation stability with the two dinonyl "isooctene"phosphonate preparations is difficult to explain since the corrosion data are quite comparable. The good oxidation and corrosion stability for the dibutyl "styrene"phosphonates is similar to that for the dibutyl benzenephosphonate.

The viscosity at -40°F was generally lower for the bottoms or technical grade product than for the pure product. The two exceptions were the dinonyl "isooctene"phosphonate and to a lesser extent, the dibutyl benzenephosphonate where the pure products were less viscous at all temperatures. In three cases the viscosity at -40°F was considerably lower for the technical grade although the viscosities at 100°F or 210°F were very similar. In the other instance, with dibutyl "styrene"phosphonate, the viscosity at -40°F, 100°F and 210°F were almost identical for both types of preparation.

C. Additive Studies

1. Thickeners and VI Improvers

Since many of the compounds prepared under this contract have relatively low viscosity but low flammability, the effect of thickeners or VI improvers has been studied.

Compounds of very low viscosity (less than 10 cs. at 100°F) have been blended with Acryloid (alkylated methacrylate polymer or copolymer) to bring the viscosity up to the aircraft hydraulic fluid range (MIL-C-5606 requires 10 cs. at 130°F or about 15 cs. at 100°F). Correspondingly, compounds of higher viscosity (20-25 cs. at 100°F) have been thickened to bring them up to SAE 10 and SAE 20 grades. The data are given in Tables 4 and 5.

The example of the first type above was dibutyl benzenephosphonate, technical-grade, which has a viscosity of 5.17 cs. at 100°F. To thicken this product to the aircraft hydraulic fluid range required 10%w Acryloid HF8125. The VI of this blend was 238, which is higher than that for a mineral oil hydraulic fluid formulated to MIL-C-5606 specification. Corrosion and oxidation of this thickened phosphonate blend, without inhibitors, were moderately low. However, an undesirable feature was the poor miscibility of the polymer with the dibutyl benzenephosphonate at temperatures below about 0°F. It was

(Tables 4 and 5 follow.)

Table 4. OXIDATION-CORROSION TESTS ON TECHNICAL-GRADE PREPARATIONS AND BLENDS WITH POLYMER AND INHIBITORS

[illegible]

Table 5. OXIDATION-CORROSION TESTS ON TECHNICAL GRADE AND DISTILLED PRODUCTS WITH INHIBITORS AND/OR POLYMERS

Spec.	Distillate α -chloroacetic phosphonate	Bottoms	Distillate α -chloroacetic phosphonate	Bottoms	Distillate α -chloroacetic phosphonate	Bottoms	Other	Pure
Reference		374-137-57		374-137-51		374-137-59		
Via. at 100°F, ca.		26.977		207A		64.82		
Via. at 100°F, ca.		26.30		13.31		8.85		
Via. at 210°F, ca.		4.33		3.16		117		
VI (D and B)		69		113		-30		
Pearl Pt., 100°F		-65		<-65		1		
Thermal 100°C, 100°F		0		9		-2		
Double-bond VI through		0		48		24		
Pipe B. at 100°F		14		15		31		
Glassware		21		22		0.72		
Oxidation		1.08		2.40		0.36		
and		0		1.05		0.04		
Corrosion		2.44		1.68		36		
P. N. Standard No.		104		1.01		37.6		
Acid Test. No.		73.8		1.05		1695		
For Polymer		1705		0.36 500W		374-137-55		
For Indicator		104-137-55		1694		1695		
Via. at 100°F		0.36 PAN		0.875 PAN		374-137-55		
Via. at 210°F		26.63		13.48		0.225 PAN		
VI		106		3.16		91.9		
Oxidation		1.08		3.17		13.15		
and		0.04		119		239		
Corrosion		0.04		8.63		0.08		
P. N. Standard No.		104		4.04		0.80		
Acid Test. No.		73.8		2.16		0.04		
For Polymer		1705		1.44		9		
For Indicator		104-137-55		1.92		0		
Via. at 100°F		0.36 PAN		7		2.5		
Via. at 210°F		26.63		1.32		4		
VI		106		65.6		4.85		
Oxidation		1.08		2.96		4.12		
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
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Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
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Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
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Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
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Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation		1.08		2.96				
and		0.04		0.04				
Corrosion		0.04		1.32				
P. N. Standard No.		104		4.5				
Acid Test. No.		73.8		1.08				
For Polymer		1705		0.36				
For Indicator		104-137-55		1.32				
Via. at 100°F		0.36 PAN		7				
Via. at 210°F		26.63		1.32				
VI		106		65.6				
Oxidation								

impossible to obtain a viscosity at -40°F on this blend since when the blend was held at this temperature, the polymer precipitated out and plugged the capillary of the viscometer. A 10% blend of Santodex (alkylated styrene polymer) in this same stock was not miscible at room temperature. It was subsequently learned that, to assure adequate miscibility with polymer at low temperature, the alkyl chain must be longer than butyl.

An attempt to improve the low temperature miscibility between polymer (Acryloid) and dibutyl benzenephosphonate was made by adding a mutual solvent such as dioctyl sebacate (Plexol 201). However, the blend (FW-1698) containing about 15% of Plexol 201 in the thickened dibutyl benzenephosphonate (FW-1690), was still not sufficiently improved in low temperature miscibility.

Both dinonyl benzenephosphonate or dinonyl "isooctene"phosphonate were readily thickened with Acryloid HF-8125 as shown by the data in Tables 4 and 5. Five per cent Acryloid HF-8125 brought both into the SAE 10 range and 10% Acryloid increased the viscosity into the SAE 20 range. Although the VI of the "isooctene"phosphonate base liquid was slightly higher than that of the benzenephosphonate (89 compared with 84), relative VI's of the blends with Acryloid were reversed (144 and 138; compared with 150 and 146). Incidentally, the viscosity and VI of the 10% blends are in the same ranges as those for the Prestone motor oil (alkylene oxide polymers).

As pointed out in the previous report, the bis $\sqrt{2}$ -(dibutyl phosphono)ethyl/ether is not miscible with Acryloid. However, the longer chain length end group in bis $\sqrt{2}$ -(dinonyl phosphono)ethyl/ether does provide satisfactory miscibility with Acryloid. Five per cent Acryloid HF-8125 in this product increased the viscosity from SAE 20 to SAE 30 while raising the VI from 117 to 132.

2. Corrosion and Oxidation Inhibitors

As mentioned previously (see V), some inhibitor studies were made on dioctyl "styrene"phosphonate. Although this compound gave a low level of oxidation and corrosion without inhibitors, it is sufficiently corrosive to cause some concern. However, since only a limited improvement was obtainable with this base, a similar Victor product, dioctyl "isooctene"phosphonate, which gave a high level of oxidation and corrosion, was thus deemed more suitable for inhibitor studies. Accordingly, a large number of phosphorus compounds as well as a few conventional inhibitors were tested in this base stock using the small scale oxidation corrosion test at 250°F (described in III). In general, each compound was first tested at 1% concentration and those which looked promising were then tested at lower concentration. The data are given in Table 6.

It is both interesting and surprising that the more promising inhibitors in this stock of dioctyl "isooctene"phosphonate, phenyl- α -naphthylamine (PAN) and 2,6-di-tert-butyl-4-methylphenol (26B4MP) were of no value in dioctyl "styrene"phosphonate (as previously discussed in V). Phenothiazine, which was also unsuccessful with dioctyl "styrene"phosphonate, was fairly

effective in the dioctyl "isooctene"phosphonate but inferior to PAN or 26B4MP. On the other hand, the combination of glycidyl phenyl ether and bis(methylene tolyl sulfide), which showed promise with dioctyl "styrene"phosphonate, doubled the copper corrosion but did decrease the degree of oxidation.

Several of the nitrogen-containing phosphorus compounds had a beneficial effect at the 1% concentration level but the effectiveness dropped off rapidly at lower concentrations. Examples in this group include dibutyl 2-diethyl-aminoethanephosphonate, dibutyl 2-morpholinoethanephosphonate, ethyl bis(2-(dibutyl phosphono)ethyl)amine and (a non-phosphorus amine) bis(2-ethylhexyl)amine. In some of the above examples, corrosion was lower at the lower concentration but oxidation was higher.

Tributyl phosphite and dibutyl diisopropylamidophosphite reduced oxidation but copper corrosion was more than doubled. Other phosphites, notably tris(7-methyl-4-thiaoctyl) phosphite, trinonyl phosphite and tris(2-ethylhexyl) phosphite lowered both oxidation and corrosion at 1% concentration but were of questionable value at 0.5% concentration (high corrosion or oxidation). Another phosphite, tris(2-chloroethyl) phosphite, reduced oxidation but increased corrosion of magnesium and cadmium as well as copper. This was the only instance where corrosion of metals other than copper reached significant values. Didecyl phosphite increased copper corrosion and had little effect on oxidation.

Triphenyl phosphine reduced copper corrosion and oxidation although not to the extent of the PAN, 26B4 MP or phenothiazine.

The following compounds had little or no inhibitor effectiveness in dioctyl "isooctene"phosphonate: diethylene glycol bis(dibutyl phosphonmethanoate), bis(dibutyl phosphono)methyl ether, dinonyl "isooctene"phosphonate, dioctyl diisopropyl phosphoric amide, tris(2-chloroethyl) phosphate and dibutyl benzenephosphonite.

Three of the above compounds which had showed some promise in dioctyl "isooctene"phosphonate were tested in the earlier batch of dioctyl "styrene"phosphonate. All three compounds, dibutyl 2-diethylaminoethanephosphonate, bis-2-ethylhexylamine and trinonyl phosphite, not only failed to inhibit oxidation or corrosion but actually increased one or both.

A new sample of dioctyl "styrene"phosphonate, also from Victor Chemical, which had much lower acidity than the earlier batch, showed excellent oxidation and corrosion stability. The data for these tests are also given in Table 6.

Inhibitor studies on the Emeryville preparations of both molecularly distilled products and the technical-grade (bottoms) samples have been continued. The data are included in Tables 4 and 5. In many cases the inhibitor was tested in the thickened oil provided that the polymer was miscible with the organo-phosphorus compounds. The results were unpredictable. Thus, 0.25% phenyl- α -naphthylamine in the 5% Acryloid HF-8125 blend in dibutyl benzenephosphonate (tech. grade) had no beneficial effect over the uninhibited blend FW-1682. In the thickened (5%) dinonyl benzenephosphonate (tech. grade) (FW-1686) the addition of 0.5% PA. dropped both oxidation and corrosion to a

(Table 6 follows.)

Table 6. OXIDATION AND CORROSION TESTS ON INHIBITED DIOCTYL-ISOCTENE-PHOSPHONATE

Additive	Inhibitor	PV Blend No.	Oxidation Corrosion Test No.	Viscosity, cp.		V.I.	Acid Meth. No.	Corrosion				Oxidation		Color Change
				100°F	210°F			Copper	Magnesium	Weight Loss, mg/cm ²	Calcium	Aluminum	\$\frac{1}{2}\$ In. V.I.O.	
None		-	270	11.91	2.73	66	0.31	8.32	0.04	0.04	0	0.04	63	Colorless to Reddish Brown
None		-	306	11.91			0.31	8.28	0.12	0.04	0	0.08	66	Almost Colorless to Reddish Brown
Phenyl-1-ethylamine	15	1650	295	12.77			1.15	0.08	0.04	0	0	0	3	Pink to Orange
	0.5	1660	305	12.76			2.12	0.04	0	0	0	0	3.5	Orange to Orange
	0.25	1675	315	12.34			0.87	0.04	0	0	0	0	2.5	Pale Purple to Yellow
	0.1	1681	325	12.36			0.36	0.28	0.04	0.04	0	0.04	3	Pale Pink to Yellow
Di-tert-butyl-4-methylamine	1.0	1692	345	12.71	2.62	61	0.36	0.32	0.08	0.12	0	0.12	3.5	Yellow to Yellow
	0.5	1690	367	12.48			0.33	0.28	0.04	0.08	0.08	0.12	3.5	Yellow to Yellow
	0.25	1695	344	12.27	2.77	65	0.36	0.12	0.08	0.04	0	0.08	4	Yellow to Yellow
	0.1	1695	363	12.44			1.21	0.48	0	0	0	0	3.87	Almost Colorless to Yellow
Dioctyl 8-allylaminophosphonate	1.0	1695	300	12.42			1.18	0	+0.16	+0.08	+0.08	+0.08	4.5	Yellow
	0.5	1678	314	12.55			0.35	0.32	0	0	0	0	39.5	Almost Colorless to Orange
Dioctyl 8-allylaminophosphonate	1.0	1659	279	12.48			1.11	0.32	0.16	0.20	0.16	0.12	7	Orange
	0.5	1654	299	12.55			1.16	0.12	0	0	0	0	9.5	Almost Colorless to Yellow
	0.25	1654	279	12.61			0.92	0.32	0	+0.08	0	0	3	Almost Colorless to Yellow
Di-tert-butylamine	1.0	1655	284	12.50			1.17	0.12	0	0	0	0	15	Almost Colorless to Reddish Brown
	0.5	1649	294	12.35			1.13	0.26	0	0	0	0	10	Almost Colorless to Yellow
	0.25	1672	304	12.77			2.14	1.72	0	0	0	0	29	Almost Colorless to Yellow
	0.1	1644	269	12.55			1.25	16.50	0.26	0.04	0.80	0.12	5	Yellow
Phenylamine	1.0	1643	288	12.95			1.11	0.24	0.08	0.04	0.04	0.08	5	Yellow to Red
	0.5	1628	303	12.69			2.02	0.24	0	0	0	0	5	Yellow to Red
	0.25	1650	271	12.50			0.87	0.32	0.04	0.04	0.04	0.08	5	Almost Colorless to Yellow
	0.1	1651	281	12.46			1.16	0.72	0.02	0.16	0.12	0.08	5	Almost Colorless to Yellow
Di-tert-butylamine	1.0	1646	301	12.48			1.19	6.40	0	0	0	0.08	47	Almost Colorless to Orange
	0.5	1642	286	12.44			1.14	0.84	0	0	0	0	5	Almost Colorless to Yellow
	0.25	1657	308	12.46			1.21	5.68	0	0	0	0.04	45	Almost Colorless to Reddish Brown
	0.1	1646	291	12.12			1.80	18.48	0	0	0.20	0.04	6	Almost Colorless to Yellow
Di-tert-butylamine	1.0	1651	296	12.46			2.11	13.04	6.44	0	7.40	0	11	Cloudy Yellow to Clear Greenish Yellow
	0.5	1648	299	12.70			1.05	2.44	0.04	0.12	0.04	0.04	3	Almost Colorless to Yellow
	0.25	1657	278	12.21			0.81	17.04	0.04	0.04	0.04	0.04	43	Almost Colorless to Reddish Brown
Di-tert-butylamine	1.0	1651	278	12.32			1.11	9.28	0.44	0	0.08	0.12	26	Yellow
	0.5	1631	273	12.32			0.82	3.56	0.04	0.08	0.16	0	27	Yellow
	0.25	1638	276	12.46			0.81	6.00	0.08	0	0.08	0.04	27	Yellow
Di-tert-butylamine	1.0	1655	276	12.44			0.85	19.64	0.12	0	0.12	0.08	26.6	Yellow
	0.5	1654	277	12.69			0.85	7.12	0.04	0	0	0.04	21	Yellow
	0.25	1654	289	12.27			1.08	14.04	0.08	0	0.04	0.04	25	Yellow
	0.1	1647	290	12.45			1.75	11.24	0.04	0	0.12	0.04	54	Yellow
Di-tert-butylamine	1.0	1645	315	29.35	4.20	0	2.08	0.08	0	0	0	0	2.5	Yellow to Yellow
	0.5	1671	314	27.13	4.00	-5	0.77	4.80	0	0	1.20	0	13	Yellow
	0.25	1671	311	26.80			0.82	5.04	0.04	0	7.84	0	14.5	Yellow to Reddish Brown
	0.1	1678	312	26.17			0.68	9.36	0.04	0	0.40	0	21	Yellow to Greenish Yellow
	0.05	1675	313	26.37			0.67	12.60	0	0	1.20	0	16.5	Yellow

low level. In the 10% Acryloid blend (FW-1691) the addition of 0.5%w of 2,6-tert-butyl-4-methylphenol had a similar effect although the copper corrosion and final acidity were somewhat higher than the PAN blend with less Acryloid. The use of 1% glycidyl phenyl ether and 0.15% bis(methylene tolyl sulfide) in the same blend (FW-1691) had very little beneficial effect (FW-1702). Earlier work on the molecularly distilled dinonyl benzenephosphonate (JWW-197-61) had shown excellent inhibition with either 0.5% PAN or 0.5% dibutyl 2-diethylaminoethanephosphonate. Oxidation was lower with the latter, while corrosion was lower with the PAN.

With the dinonyl "isooctene"phosphonate, technical grade, the corrosion without polymer or inhibitor was much lower than with the corresponding benzenephosphonate but the oxidation was very high. The blend containing 10% Acryloid HF-8125 (FW-1689) was used for inhibitor studies. In this blend 0.5% PAN or 0.5% 2,6-di-tert-butyl 4-methylphenol gave excellent results but again the blend of glycidyl phenyl ether and bis(methylene tolyl sulfide) was very poor.

In the bis[2-(dinonyl phosphono)ethyl]ether, tech. grade, however, none of the above three inhibitors was effective; in fact, both oxidation and corrosion were increased through the addition of the inhibitor.

In the bis[2-(dibutyl phosphono)ethyl]ether, molecularly distilled, the addition of 0.25% phenyl- α -naphthylamine to the blend containing 5% Acryloid HF-8125 (FW-1683) dropped the oxidation a small amount but corrosion was increased slightly, although possibly within the limit of reproducibility of the test. However, the low oxidation and corrosion of the thickened blend (FW-1683) in comparison to the original compound appears unusual since the polymer usually increases oxidation and corrosion if there is any change.

Thus, the amine or phenol type inhibitors look promising for dioctyl "isooctene"phosphonate, dinonyl "isooctene"phosphonate, dinonyl benzenephosphonate and bis[2-(dinonyl phosphono)ethyl]ether (all containing relatively large alkyl groups). They had little or no effect on thickened dibutyl benzenephosphonate while with bis[2-(dibutyl phosphono)ethyl]ether and dioctyl "styrene"phosphonate these inhibitors were worse than the uninhibited blends. In these instances the alkyl group was small (n-butyl) or the aromatic portion was large ("styrene"), offsetting the effect of the larger alkyl group.

MOTOR LABORATORY EVALUATIONSI. Introduction

It was considered advisable to obtain preliminary operating experience with materials covering a wider viscosity range than afforded by the two reference fluids listed in Table 10 of V-28. Three other commercially available compounds were selected, therefore, and are described, together with the original fluids and a second batch of dioctyl "styrene"phosphonate, in Table 7, following:

Table 7. PROPERTIES OF REFERENCE FLUIDS

Name	Fluid No.	Source	Viscosity (cs.)		V.I. (Dean and Davis)	Acid No. (mg. KOH/g.)	Pour Point (°F)	Micro- ¹⁾	
			100°F	210°F				Flash Point (°F)	Fire Point (°F)
HVI 100 Neutral	K-1500	Shell Oil Co.	21.78	4.11	96	0	+10	400	445
Dioctyl "styrene"phosphonate (Batch 1)	K-1508	Victor Chem.	27.13	4.02	-1	0.77	-55	435	505
Dioctyl "styrene"phosphonate (Batch 2)	K-1526	"	29.35	4.20	0	0.02	-55	435	520
Dioctyl "isooctene"phosphonate	K-1530	"	11.91	2.73	66	0.31	-70	385	465
Tricresyl phosphate	K-1517	Monsanto Chem.	29.35	4.08	-39	0.09	-15	510	> 690
Trioctyl phosphate	K-1542	Carbide & Carbon	8.22	2.26	90	0.20	< -85	410	400

1) Procedure described in Report VII-18.

None of the materials synthesized under the contract has as yet been evaluated in the Motor Laboratory, but the larger batch preparations presently underway in Experimental Plants Department will make such studies possible.

II. Orientation Studies of Reference Materials

A. Pesco Gear Pump Tests

In the pump tests reported previously (V-28) a large wear differential was noted between the mineral oil (low wear) and the phosphonate (high wear) reference fluids. Following replacement of the moving parts of the pump, however, both the general wear level and the wear differential were appreciably reduced (see Table 8). Possible differences in the composition and heat treatment of the gears may account for the change.

The new reference fluids investigated, namely, tricresyl and trioctyl phosphates, and dioctyl "isooctene"phosphonate (Tests WI-163, 164, 166 and 168, respectively) all gave low wear and little change in physical properties. Duplicate runs of the original reference materials HVI 100 Neutral and dioctyl "styrene"phosphonate, produced erratic wear results (Tests WI-161, 162, 165, 167, 169 and 170), although, again, the physical properties of the fluids were little affected.

Two factors probably contribute toward the apparent irreproducibility of wear in the Pesco apparatus. The first is the rather short duration of the test (13 hours), which allows wearing-in phenomena to exert undue influence on the total wear. The other factor is a probable carry-over from one test to the next of the anti-wear effects of phosphorus-containing films on the metal surfaces. Since extended investigation and correction of these problems are beyond the scope of the contract, wear figures from this short-time Pesco pump test will be considered to have little significance unless very large differences are observed.

With wear a secondary factor, the main purpose of the Pesco pump test will be to detect evidences of fluid deterioration by oxidation and shear breakdown. In this regard the most significant fluid alteration occurring in the ten tests reported in Table 8 was observed in Test WI-168, where dioctyl "isooctene"phosphonate increased 5% in viscosity at 100°F (as opposed to viscosity decreases in the nine other tests) and experienced the only appreciable increase in acid number (0.31 to 1.39).

B. Lauson Engine Tests - Cold Conditions

The first of two test procedures employing a small, single-cylinder, liquid-cooled, four-stroke cycle gasoline engine (Lauson Model LF; bore 2.6 in., stroke 2.5 in.) is used to study the effects of moderately cold operation upon both the lubricant and the engine. The test conditions, under the designation LA-FLL, are outlined in Table 9. Upon completion of the 40-hour test the used lubricant is examined analytically, and the oil consumption and the weight loss of the connecting rod bearing (steel-backed copper-lead) are measured. The piston skirt is given a lacquer rating (using the scale 0 to 10, where 10 represents the clean or perfect condition). Piston ring sticking, scuffing, and other pertinent phenomena are also reported when observed.

Table 8. COMPOSITION AND TEST RESULTS OF FLUIDS INVESTIGATED IN THE HIGH PRESSURE GEAR PUMP

Test Designation: PP-81 Test Conditions: Outlet Pressure, 1,000 psi. Fluid Charge, 750 ml.
 Pump Model: Peeco IP-34D Inlet Temperature, 200°F Duration, 13 hours
 Pump Speed, 1,800 rpm.

Test No. (PP-81-)	Fluid No. (E-)	Composition	Viscosity Index (Dean and Davis)	Viscosity at 100°F (cp.)		Per Cent Viscosity Change (at 100°F)	Acid Neut. No. (mg. KOH/g.)		Gear Set No.	Weight Losses (mg.)		Remarks
				New Oil	Used Oil		New Oil	Used Oil		Gears (Steel)	Bushings (Bronze)	
141	1500	W1 100 Neutral	96	21.8	21.0	-3.7	0	0	20	2.6	-	Reference run on new gears and bushings.
162	1508	Diethyl "styrene" phosphonate (Batch 1)	-1	27.1	26.3	-3.0	0.77	0.88	20	6.7	-	New gears apparently less wear-sensitive than Gear Set No. 19 (See Tests 151 and 153, Table II, V-30.)
163	1517	Tricresyl phosphate	-39	29.4	28.7	-2.4	0.09	0.15	20	2.8	-	First of a series of tests of additional reference materials.
164	1517	Tricresyl phosphate	-39	29.4	28.5	-3.1	0.09	0.14	20	0.6	-	
165	1500	W1 100 Neutral	96	21.8	20.9	-4.1	0	0	20	0.7	-	Mineral oil reference run.
166	1542	Tricresyl phosphate (Floral TOS)	90	8.2	8.0	-2.4	0.20	0.15	20	4.4	-	
167	1528	Diethyl "styrene" phosphonate (Batch 2)	0	29.4	27.9	-5.1	0.02	0.11	20	2.0	2.3	
168	1530	Diethyl "octene" phosphonate	66	11.9	12.5	+5.0	0.31	1.39	20	1.8	1.8	Increase in viscosity and Acid No. indicate fluid deterioration.
169	1508	Diethyl "styrene" phosphonate (Batch 1)	-1	27.1	26.1	-3.7	0.77	0.92	20	1.0	2.0	Note change in wear level as compared with Test 162 above.
170	1500	W1 100 Neutral	96	21.8	21.4	-1.8	0	0	20	0.7	-0.1	

Since the considerable background of data that exists for this test procedure was obtained with higher viscosity oils (approximately 130 centistokes at 100°F), connecting rod bearing weight losses with the lower viscosity reference fluids (20-30 cs. at 100°F) might reasonably be expected to be greater than the rough acceptance level of 10 mg. customarily used. Unless further tests indicate to the contrary, however, the 10 mg. wear criterion will continue, particularly since a bearing wear figure of only 4.5 mg. was obtained with the reference mineral oil, HVI 100 Neutral (Test FLI-1306, Table 9). An attempt to run trioctyl phosphate, an 8.2 centistoke fluid (at 100°F), failed after 14 hours by excessive wiping of the connecting rod bearing (Test FLI-1315, Table 9). The pistons ranged from very dirty, for dioctyl "styrene"phosphonate (Test FLI-1310), to extremely clean, for tricresyl phosphate (Test FLI-1311). The connecting rod bearing weight loss was low, as mentioned above, for the mineral base reference oil, but high for all the phosphorus compounds. The sharp drop in used oil viscosity reported for the four tests that reached completion is undoubtedly the result of crankcase dilution. Increase in acidity was more pronounced for the phosphorus compounds than for the mineral oil, thus correlating with bearing weight loss.

C. Lauson Engine Tests - Hot Conditions

For small-scale high temperature engine evaluation of crankcase lubricants This Laboratory employs the research version of the Lauson engine (Model H2, bore 2-5/8 in., stroke 2-3/4 in.). Except for the different operating conditions, as outlined in Table 10, the test is conducted and reported in a manner identical to that described previously for the cold Lauson test.

Lubricants that survive the milder Cold Conditions engine test (IA-FLI) and appear promising in bench scale studies are subjected to the hot test (IE-LIS). In the three reference tests reported to date (Table 10), the cleanest piston and the lowest connecting rod bearing weight loss were obtained with the newer batch of dioctyl "styrene"phosphonate (Test LIS-141). The fact that the used fluid from this test showed the greatest increase in acid number (from 0.02 to 32.5) is hardly compatible with the low bearing weight loss, unless the decomposition products formed a protective coating on the bearing surface. The bearing weight losses sustained with the HVI 100 Neutral mineral oil and with tricresyl phosphate (Table 10, Tests LIS-137 and 144) were higher than the customary acceptance level of about 100 mg., established as in the case of the cold Lauson test, with higher viscosity oils. The results of the three tests reported in Table 10 vary widely and appear to reverse many of the observations of the cold Lauson tests (Table 9). Some of the runs will be repeated, therefore, in order to check the validity of the limited data reported herein. Severe oxidation of the used fluid occurred in all three tests, as evidenced by substantial increases in used oil viscosity.

The contrast in piston skirt cleanliness between a relatively dirty and an exceptionally clean piston is evident in the photographs of Figures 2 and 3, following, representing Tests LIS-137 and 141, respectively.

(Figures 2, 3, 4 and 5 follow.)
(Tables 9 and 10 follow.)

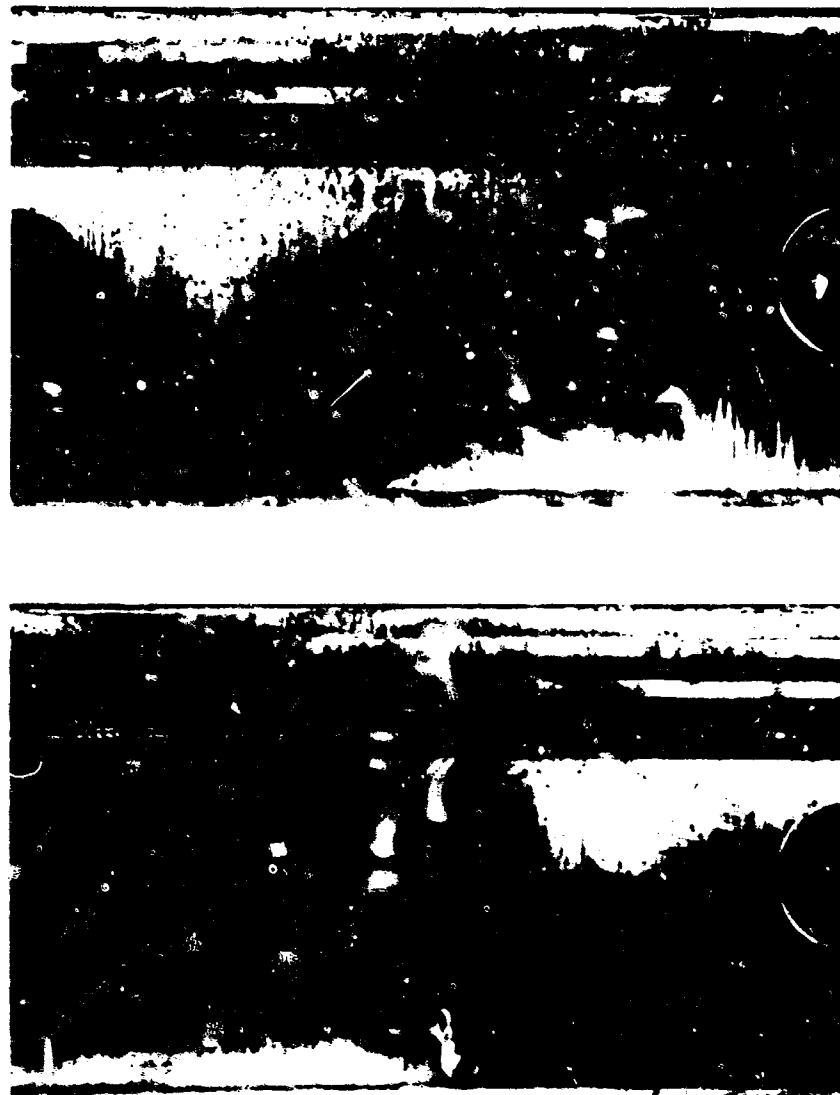


Figure 2. DEVELOPED VIEWS OF PISTON SKIRT, SHOWN WITH
THRUST SIDE AT TOP, FROM TEST LH-LIS-137

Lubricant: HVI 100 Neutral Oil

Lacquer Rating: 3.67 (0 = completely black)



Figure 3. DEVELOPED VIEWS OF PISTON SKIRT, SHOWN WITH
THRUST SIDE AT TOP, FROM TEST LH-LIS-141

Lubricant: Dioctyl "styrene"phosphonate (Batch 2)
Lacquer rating: 9.47 (10 = clean)

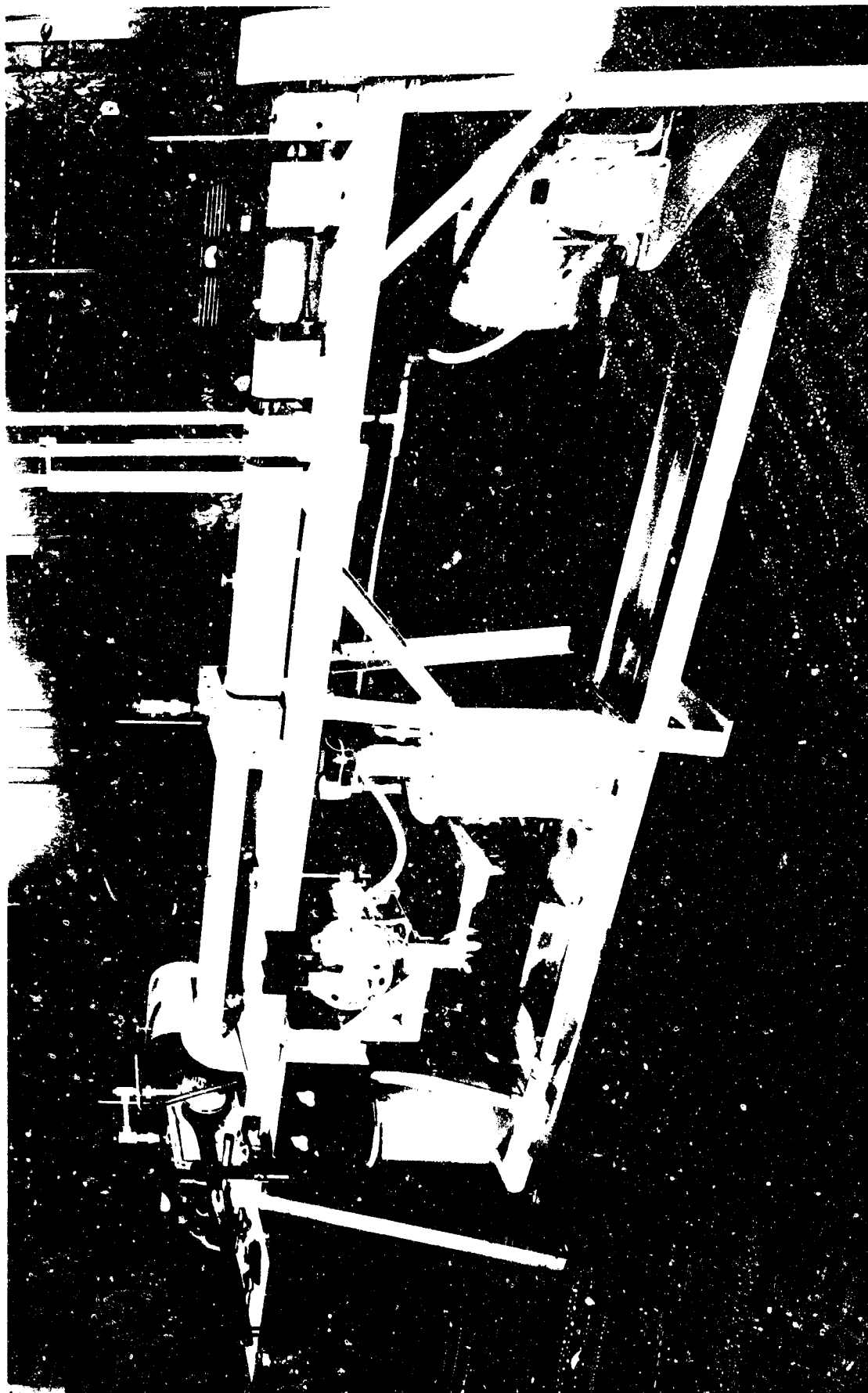


Figure 4. SPUR GEAR MACHINE

Figure 5. SCHEMATIC DIAGRAM OF SPUR GEAR MACHINE

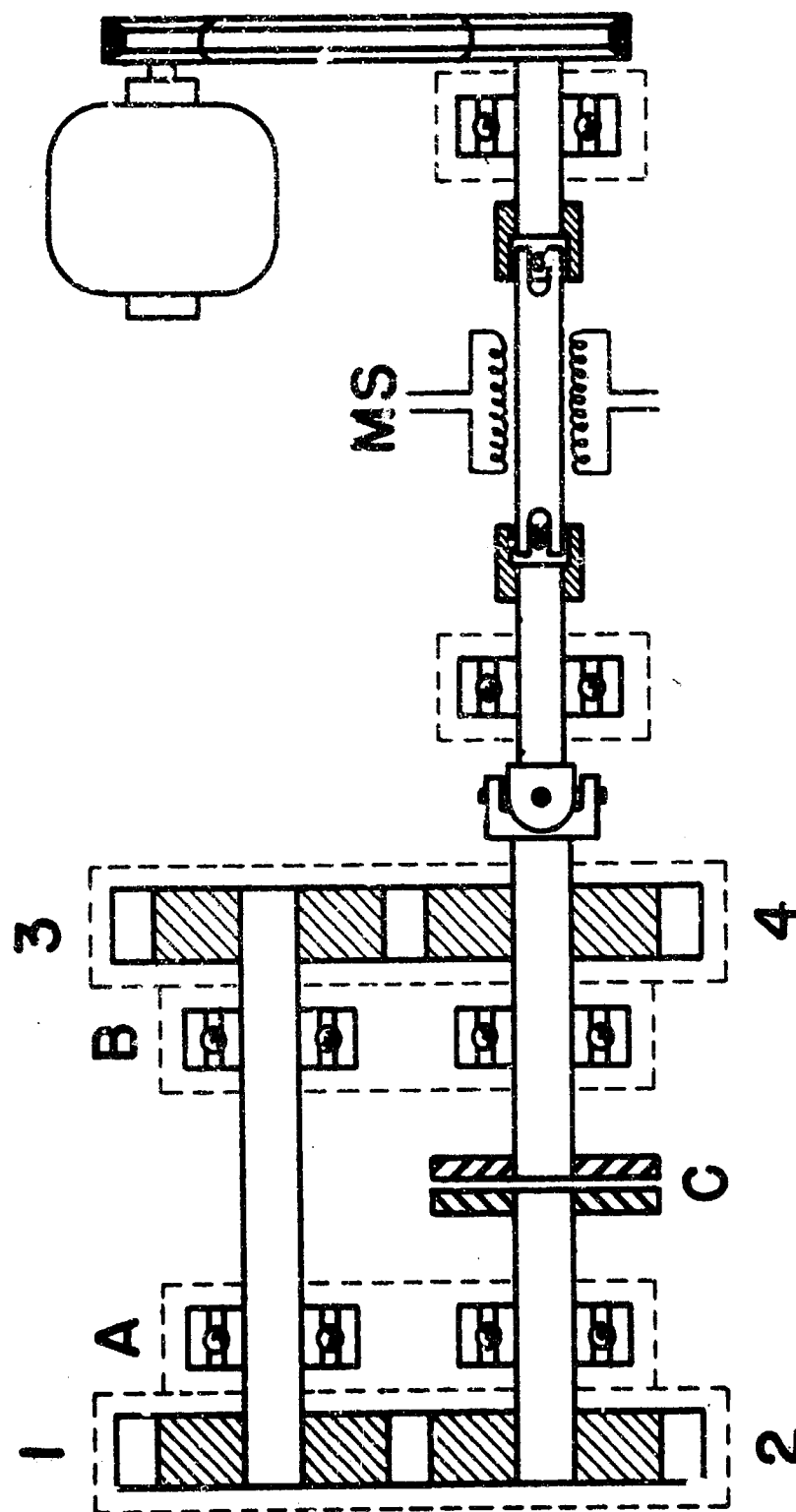


Table 9. SUMMARY OF TEST RESULTS OF FLUIDS INVESTIGATED IN THE LAUSON ENGINE: COLD CONDITIONS.

Test Designation: 1A-711 Engine Model: 1F (Single Cyl.) Bore and Stroke: 2.6 in. x 2.5 in.										Test Conditions: Speed, 1675 rpm. Load, 1 kw. Duration, 40 hr. Oil Charge, 700 ml.				Oil Temp., 195°F Jacket Temp., 86°F In 95°F Out		Fuel, Regular Grade-Automotive F-A Ratio, Max. Power			
Test No. (1A-711-)	Fluid No. (K-)	Composition	Test Duration (Hours)	Lacquer Rating (0-Black, 10-Clean)	Oil Consumption (ml./hr.)	Con. Rod Bearing Weight Loss (gr.)	Power Output at End of Test (kw.)	Oil Viscosity (sg.)				Viscosity Index (Dean-Davis)				Acid Neut Mo. (mg. KOH/g.)		Remarks	
								100°F		210°F		New Used		New Used		New Used			
1316	1300	SVI 100 Neutral	40	7.66	0.2	4.5	1.00	21.8	11.4	4.1	2.8	96	103	0	0.4	0	0.4	Mineral oil reference run.	
1310	1308	Dioctyl "styrene" phosphate (Batch 1)	40	0.85	0.0	48.2	0.95	27.1	15.0	4.0	3.0	-1	42	0	0.77	4.6	0.77	4.6	Commercial phosphate reference run.
1311	1317	Tricresyl phosphate	40	9.65	1.5	16.7	0.75	29.4	21.1	4.1	3.6	-39	25	0	0.09	2.8	0.09	2.8	Commercial phosphate reference run.
1314	1306	Dioctyl "styrene" phosphate (Batch 2)	40	4.05	-	35.0	0.85	29.4	15.8	4.2	3.1	0	36	0	0.02	5.3	0.02	5.3	Test of newer (Lower Acid No.) batch of material run in Test No. 1310, above.
1315	1342	Tricresyl phosphate (Fluorol TUF)	14	5.30	-	1,793.5	1.00	8.2	7.0	2.3	2.1	90	101	0	0.20	1.1	0.20	1.1	Attempt to run a very low viscosity phosphate. Failed by excessive wiping of connecting rod bearing (copper-lead).

Table 10. SUMMARY OF TEST RESULTS OF FLUIDS INVESTIGATED IN THE LAUSON ENGINE: HOT CONDITIONS.

Test Designation: 12-115 Engine Model: H2 (Single Cyl.) Bore and Stroke: 2-5/8 in. x 2-3/4 in.										Test Conditions: Speed, 1020 rpm. Load, 0.6 hr. Duration, 60 hr. Oil Charge, 1020 ml.				Oil Temp., 300°F Jacket Temp., 370°F Fuel, Chem. 1A Specification F-A Ratio, Max. Power						
Test No. (12-L.N.-)	Fluid No. (K-)	Composition	Test Duration (Hours)	Vacuum Rating (0-Black, 10-Clean)	Oil Consumption (ml./hr.)	Con. Rod Bearing Weight Loss (gr.)	Power Output at End of Test (hr.)	Oil Viscosity (cg.)				Viscosity Index (Dean-Davis)				Acid Neut. No. (mg. KOH/g.)				Remarks
								100°F		210°F		New Used		New Used		New Used		New Used		
								New Oil	Used Oil	New Oil	Used Oil	New Oil	Used Oil	New Oil	Used Oil	New Oil	Used Oil	New Oil	Used Oil	
137	1300	WVI 100 Neutral	60	3.67	3.3	654.5	0.6	21.8	31.4	4.1	5.1	96	101	0	4.1	0	4.1	0	4.1	Mineral oil reference run.
141	1306	Dioctyl "styrene" phosphate (Batch 2)	60	9.47	2.0	10.5	0.6	29.4	48.7	4.2	6.0	0	64	0.32	32.5	0.32	32.5	0.32	32.5	Commercial phosphate reference run.
144	1317	Tricresyl phosphate	60	8.18	2.6	377.1	0.6	29.4	28.6	4.1	7.8	-39	107	0.09	3.3	0.09	3.3	0.09	3.3	Commercial phosphate reference run.

D. Spur Gear Load Carrying Capacity Tests

The ability of a lubricant to prevent metal-to-metal contact between the mating surfaces of loaded gears, and thus to prevent scoring, can be assessed in the Spur Gear Machine, shown in Figure 4. The four-square principle of loading is used, as depicted schematically in Figure 5, permitting the load transmitted through the gear teeth to be raised by measured increments until scoring is observed. The gear geometry and material specifications and the operating conditions of the test are summarized in Table 11, following:

Table 11. LOAD CARRYING CAPACITIES OF FLUIDS INVESTIGATED
IN THE SPUR GEAR LUBRICANTS TESTING MACHINE

Test Designation: GS-LC2
Gears: Diametral pitch, 6.
Pressure angle, 20°.
Face width, 0.250 in.
Center distance, 3 in.
No. of teeth, -
Pinion, 17.
Gear, 19.
Steel, SAE 3312.
Hardness, -
Case, 32 Rockwell C.
Core, 30-40 Rockwell C.

Test Conditions: Shaft speed, 3000 rpm.
Load increments, 5 lb. beam load.
Duration of each load, 5 min.
Test length, until scoring.
Oil temp., approx. 100°F.
Oil flow rate, 10 ml./sec.
Oil charge, 1000 ml.

Test No. (GS-LC2-)	Fluid No. (K-)	Composition	Load at Initial Scoring		Remarks
			Lbs. Beam Load	Hp.	
446	1500	HVI 100 Neutral	5	3.8	Mineral oil reference run.
447	1526	Diocetyl "styrene" phosphonate (Batch 2)	20	23.3	Commercial phosphonate reference run.
448	1500	HVI 100 Neutral	2	2.3	Repeat of Test 446 at lower starting load.
449	1517	Tricresyl phosphate	2	2.3	Commercial phosphate reference run.
450	1542	Triocetyl phosphate	50+	58.3+	Incipient scoring at load limit of gears.
451	1530	Diocetyl "iso-octene" phosphonate	45+	52.5+	Extraneous bearing failure stopped test.

Minimum load carrying capacities (5 lb. beam load or less) were recorded for the HVI 100 Neutral oil and tricresyl phosphate, as shown in Table 11, Tests LC2-446 and 449. Intermediate results were obtained from dioctyl "styrene"phosphonate (Test LC2-447), while trioctyl phosphate and dioctyl "isooctene"phosphonate both approached the strength limit of the gear teeth with only incipient scoring noted. It might be expected that the more corrosive materials would allow higher loads by forming low shear strength, i.e., Extreme Pressure, corrosion products on the faces of the gear teeth. Results of the Small Scale Oxidation and Corrosion Test (as reported under Bench Scale Evaluations) which show trioctyl phosphate and dioctyl "isooctene" phosphonate to be markedly more corrosive than the other materials in Table 11, offer substantiation for the E.P. hypothesis.

III. Expansion of the Evaluation Program

The Motor Laboratory orientation program, prior to the evaluation of specific contract preparations, is currently being broadened by 1) submitting the reference materials, in the neat or uncompounded state, to a more diversified test program as indicated in III-26, 27 and, 2) instituting a limited study of the reference fluids when used in conjunction with minor proportions of such additive materials as oxidation and corrosion inhibitors, and viscosity index improvers.

ly

William E. Vaughan
as Coordinator

Appendices A, B and C

APPENDIX A

On November 6, 1950, a conference on the Contract work to that date was held at the Office of Naval Research, Washington, D. C. Present at the conference were the following:

Admiral T. A. Solberg,	USN, ONR, (Part time)
Messrs. S. A. Ballard,	Shell Development Co.
R. E. Fox,	NRL
U. E. Hanninen,	NRL
E. Margolin,	AMC
C. M. Murphy,	NRL
R. Roberts,	ONR
F. Schulman,	ONR
L. A. Shinn,	ONR
C. C. Singleterry,	BuAir
H. K. Sutherland,	Shell Development Co.
H. A. Tannett,	NRL
W. E. Vaughan,	Shell Development Co.
W. A. Zisman,	NRL

The past work was reviewed and plans for the future (and the experimental data justifying the plans) were discussed. The Navy's representatives voiced constructive comment along several lines, including the following:

- (1) Possible modification of the Bestian reaction for use in synthesis;
- (2) Correlation of pipe cleaner and flash point flammabilities with oxygen demand and spontaneous ignition temperatures;
- (3) Possibilities for application in aircraft turbine lubricants;
- (4) Effect of the most promising compounds on materials of construction other than those used in the corrosion tests, such as titanium and rubbers. Another conference will probably be held in the Spring, 1951, as it was the consensus of opinion that the meeting was highly profitable.

APPENDIX B

FORMULA INDEX FOR COMPOUNDS DISCUSSED IN THIS REPORT

Empirical Formula	Name	Structural Compound	Pure	Reference to Preparation, Page No. Tech
C ₁₀ H ₁₃ Br ₂ O ₃ P	bis(2-bromoethyl) benzenephosphonate	(BrC ₂ H ₄ O) ₂ PO-C ₆ H ₅	3	
C ₁₀ H ₁₃ Cl ₂ O ₃ P	bis(3-chloroethyl) benzenephosphonate	(ClC ₂ H ₄ O) ₂ PO-C ₆ H ₅	3	
C ₁₄ H ₂₂ ClO ₂ P	butyl p-chlorobenzene(butane)phosphinate	(C ₄ H ₉ O)(ClC ₆ H ₄)(C ₄ H ₉)PO		6
C ₁₄ H ₂₃ O ₃ P	dibutyl benzenephosphonate	[(C ₄ H ₉ O) ₂ PO-C ₆ H ₅]		6
C ₁₆ H ₂₅ O ₃ P	dibutyl "styrene"phosphonate	(C ₄ H ₉ O) ₂ PO-C ₆ H ₇	4	
C ₁₇ H ₂₇ O ₃ P	dibutyl nonanephosphonate	(C ₄ H ₉ O) ₂ PO-C ₉ H ₁₉	3	
C ₂₀ H ₄₄ O ₇ P ₂	bis[2-(dibutyl phosphono)ethyl]ether	[(C ₄ H ₉ O) ₂ PO-C ₂ H ₄] ₂ O		7, 8
C ₂₁ H ₄₅ O ₆ P ₂	pentamethylene tetra-n-butyl diphosphate	[(C ₄ H ₉ O) ₂ P-PC ₂ H ₄] ₂ CH ₂		
C ₂₂ H ₃₉ O ₃ PS ₂	bis(7-methyl-4-thiaoctyl) benzenephosphonate	(C ₅ H ₁₁ SC ₃ H ₆ O) ₂ PO-C ₆ H ₅		7
C ₂₂ H ₄₅ O ₆ P ₂	bis-1,2-(dibutyl phosphonoethoxy)ethane	[(C ₄ H ₉ O) ₂ PO-C ₂ H ₄ -O-CH ₂] ₂	4	
C ₂₄ H ₃₇ O ₇ P ₂	bis[2-(butyl p-chlorobenzenephosphinico)-ethyl]ether	[(C ₄ H ₉ O)(ClC ₆ H ₄)PO-C ₂ H ₄] ₂ O		
C ₂₄ H ₄₁ O ₃ P	dioctyl "styrene"phosphonate	(C ₈ H ₁₇ O) ₂ PO-C ₆ H ₇		
C ₂₄ H ₄₃ O ₃ P	dinonyl benzenephosphonate	(C ₉ H ₁₉ O) ₂ PO-C ₆ H ₅	4	
C ₂₄ H ₄₃ O ₇ P ₂	bis[2-(dibutyl phosphono)butyl]ether	[(C ₄ H ₉ O) ₂ PO-C ₄ H ₉] ₂ O	5	6
C ₂₆ H ₄₉ O ₆ F ₃	bis[2-(dibutyl phosphono)ethyl] benzene-phosphonate	[(C ₄ H ₉ O) ₂ PO-C ₂ H ₄ O] ₂ -PO-C ₆ H ₅	5	
C ₂₈ H ₅₃ O ₃ P	dinonyl "isooctene"phosphonate	(C ₉ H ₁₉ O) ₂ PO-C ₆ H ₁₅		6, 7
C ₂₇ H ₅₇ O ₃ P	trinonyl phosphite	(C ₉ H ₁₉ O) ₃ P	2	
C ₄₀ H ₈₄ O ₇ P ₂	bis[2-(dinonyl phosphono)ethyl]ether "chloroperaffin"phosphonate	[(C ₉ H ₁₉ O) ₂ PO-C ₂ H ₄] ₂ O	4	
--	--	--	5	

Note: Nonane and nonyl refer to 3,5,5-trimethylhexane and 3,5,5-trimethylhexyl respectively.

APPENDIX C

PERSONNEL

Following is a list of the professional personnel who have been actively associated with the contract work of the quarter covered by this report (including both full- and part-time participation):

Preparations:

S. A. Ballard
R. C. Morris
J. L. Van Winkle
W. E. Vaughan, Coordinator

Bench Scale Evaluations:

R. G. Larsen
W. F. Ross
S. K. Talley
F. J. Watson

Motor Laboratory Evaluations:

A. G. Cattaneo
A. R. Isitt
J. E. Weigel

Analytical Work:

G. W. Bond
F. R. Brooks
A. E. O'Donnell
E. D. Peters